165584

URS

October 30, 2001

Mr. Mike Ribordy
U.S. EPA – Region 5
77 West Jackson Boulevard (SR-6J)
Chicago, IL 60604-3590

RE: Sauget Area 2 Sites **Deliver by Overnight Mail**

Dear Mike:

This letter is intended to resolve and clarify several issues that have been raised by Mr. Richard Byvik in his review of the Sauget Area 2 Quality Assurance Project Plan (Volume 2B). Specifically, this letter addresses Item Number 4 in Mr. Byvik's most recent comments, which relates to Appendix L, Air Sampling Methods. Based upon a review of the most current information, the following methods will be utilized for the sampling and analysis of air samples for the specified parameters:

VOCs - TO15

This is a modification from the original plan, which had specified Method TO1. A copy of Severn Trent Laboratories (STL) standard operating procedure (SOP) for TO15 (SOP No. LM-AT-TO15) including target compounds and associated reporting limits, was previously supplied to USEPA on September 7, 2001.

SVOCs - TO13

This is consistent with the original plan, and a copy of STL's SOP for TO13 (SOP No. AR:01:21:98:1) was previously supplied to USEPA on September 7, 2001. This SOP is applicable for Methods TO4, TO10, and TO13. Please note that Method TO13 is applicable only for PAH compounds. A table listing the target analytes and their associated reporting limits for this method is enclosed.

Pesticides - TO4

This is a modification from the original plan, which had specified Method TO13. A copy of STL's SOP for TO4 (SOP No. AR:01:21:98:1) was previously supplied to USEPA on September 7, 2001. This SOP is applicable for Methods TO4, TO10, and TO13. A table listing the target analytes and their associated reporting limits for this method is enclosed.

URS Corporation
2318 Millpark Drive
Maryland Heights, MO 63043
Tel: 314.429.0100
Fax: 314.429.0462

URS

Herbicides – NA

Upon review of the commercially available, approved sampling and analysis methods for air samples, we do not believe that there is currently a method available which is suitable for the analysis of herbicides. Therefore, this group of compounds will be deleted from the air-sampling program.

PCBs – TO4

This is a modification from the original plan, which had specified Method TO13. A copy of STL's SOP for TO4 (SOP No. AR:01:21:98:1) was previously supplied to USEPA on September 7, 2001. This SOP is applicable for Methods TO4, TO10, and TO13. A table listing the target analytes and their associated reporting limits for this method is enclosed.

Dioxin – TO9

This is consistent with the original plan. A copy of STL's SOP for Method 8290 (SOP SAC-ID-0005) was previously supplied to USEPA on October 15, 2001. This SOP is also used for ambient air samples (TO-9). The following sections pertain specifically to ambient air analyses: 2.3, 3.6, 7.8, 7.10, 8.3, 9.7, 11.4.16 and 17.1.9.

Metals – PM2.5/IO3.1

This is consistent with the original plan. A copy of URS' SOP for Method PM2.5 is enclosed, as are STL SOPs ME54:10:29:01:1 (Digestion and Preparation Procedures for Metals in Air) and ME70:03:07:01:7 (Elements by ICP – 200.7 and 6010B). A table listing the target analytes and their associated reporting limits for this method is enclosed.

I trust that this information resolves any outstanding issues as they pertain to approval of the QAPP for this program. Please do not hesitate to call Steve Smith if you have any questions on this information.

Sincerely,

Robert B. Veenstra
Principal

cc: Steve Smith, SA2SG Project Manager

STL Savannah

Air Parameters

PARAMETER	RL(ug)
Metals by IO-3(6010B)	
Aluminum	4
Antimony	1.2
Arsenic	0.2
Barium	4
Beryllium	0.1
Cadmium	0.1
Calcium	100
Chromium	0.2
Cobalt	1
Copper	0.5
Iron	2
Lead	0.06
Magnesium	100
Manganese	0.3
Nickel	0.8
Potassium	100
Selenium	0.1
Silver	0.2
Sodium	100
Thallium	0.2
Vanadium	1
Zinc	0.4
PAH by TO13(8270C)	
Acenaphthene	10
Acenaphthylene	10
Anthracene	10
Benzo(a)anthracene	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(g,h,i)perylene	10
Benzo(a)pyrene	10
Chrysene	10
Dibenz(a,h)anthracene	10
Fluoranthene	10
Fluorene	10
Indeno(1,2,3-cd)pyrene	10
Naphthalene	10
Phenanthrene	10
Pyrene	10

PARAMETER	RL(ug)
Pesticides by TO4(8081A)	
Aldrin	0.050
alpha BHC	0.050
beta BHC	0.050
delta BHC	0.050
gamma BHC (Lindane)	0.050
alpha Chlordane	0.050
gamma Chlordane	0.050
4,4'-DDD	0.10
4,4'-DDE	0.10
4,4'-DDT	0.10
Dieldrin	0.10
Endosulfan I	0.050
Endosulfan II	0.10
Endosulfan sulfate	0.10
Endrin	0.10
Endrin aldehyde	0.10
Endrin ketone	0.10
Heptachlor	0.050
Heptachlor epoxide	0.050
Methoxychlor	0.50
Toxaphene	5.0
PCBS by TO4(EPA 680)	
Monochlorobiphenyls	0.10
Dichlorobiphenyls	0.10
Trichlorobiphenyls	0.10
Tetrachlorobiphenyls	0.20
Pentachlorobiphenyls	0.20
Hexachlorobiphenyls	0.20
Heptachlorobiphenyls	0.30
Octachlorobiphenyls	0.30
Nonachlorobiphenyls	0.50
Decachlorobiphenyl	0.50
RL = reporting limit	

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DIGESTION AND PREPARATION PROCEDURES FOR METALS IN AIR

Approved by:

R Wayne Rollins — 29 October 2001

Date

Title: Technical Manager, QA

STL X Savannah ___ Tallahassee ___ Mobile ___ Tampa West

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures used to prepare and digest air samples collected on filter paper prior to the analysis by ICP (SOP ME70). This preparation may be performed on samples tested for Suspended Particle Matter (SPM). However, the gravimetric determination of SPM is beyond the scope of this procedure.

2.0 SUMMARY OF METHOD AND DEFINTIONS

2.1 An ambient air sample is routinely collected on 8" x 10" quartz/glass fiber filter paper. A 1" x 8"strip of the filter is removed and placed in a digestion vessel. A nitric acid/hydrochloric acid extraction solution is added and the sample is digested for 20 minutes. After cooling, 10mL of deionzed water is added and the sample is allowed to stand for 30 minutes. The digest is filtered, adjusted to a final volume of 20mL, and analyzed by ICP (Method 6010B, SOP ME70). The results are reported as micrograms of metal on the filter paper.
Definitions

Digestate - the digested sample
ICP - inductively coupled (argon) plasma
HCl --hydrochloric acid
HNO3 -- nitric acid

2.3 The SOP is based on the guidance in Compendium Method IO-3.1 and SW-846 Method 6010B.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The samples are digested in strong acid solutions and contain acid concentrations of 10-20% by volume. The analyst must wear protective clothing such as a lab coat or apron. The acids used in this procedure will destroy unprotected clothing. The analyst must wear proper eye protection such as lab glasses or face shield. Acid can be splashed into the eyes from many sources. Gloves must be worn to protect hands from acid burns.

3.3 The acid digestion procedures must be performed under a properly functioning fume hood. The acid fumes from the digestion can cause mild to severe respiratory problems if breathed.

3.4 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.5 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.6 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses and the safe handling instructions for these compounds.

3.7 Care must be taken when handling the digestion beakers. Before handling a vessel that has been in use, check the temperature to make sure that it is not hot. Make sure that the digestion vessels are placed on a stable platform during and after the digestion. Vibrations from the hood or an unstable platform can cause the beakers to move and possibly to fall and splatter an analyst with a hot acid solution. Hot acids can cause severe skin burns and destroy unprotected clothing.

4.0 INTERFERENCES

Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Ambient quartz filters should be received folded in half lengthwise with the particulate material inward and enclosed in protective envelopes. Some filters may be provided in a shipping envelope with an unused filter covering the exposed surface. At least one blank filter must also be received for use as the blank and the lab control sample. If one or more blank filters are not received, notify the project manager immediately.

Inspect the filters upon receipt into the preparation lab for tears or holes in the filters. Note if any of the particulate material has fallen off of the filter. Capture any "loose particulate material in a tared plastic container. Notify the project manger via an Anomaly Report.

Check the identification of the filter. If any discrepancy is noted or if the filter cannot be unambiguously identified, notify the project manger via an Anomaly Report.

The samples are stored at ambient (room) temperature and must be prepared and analyzed within 180 days of collection.

6.0 APPARATUS AND MATERIALS

6.1 Hot plate or digestion block-capable of maintaining a sample temperature of 95C+/-5C. The temperature of the hot plate or digestion block must be monitored and recorded each day samples are digested. The temperature is measured in a beaker or digestion vessel containing reagent water.

6.2 Digestion vessels, appropriate volume for use with digestion block

6.3 Teflon or Pyrex beakers, appropriate volumes, Recommend 150mL or 250mL beakers for use with hot plates

6.4 Watch glasses, for use with beakers (block digestion vessels do not require watch glasses)

6.5 Teflon vials-25mL

6.5 Volumetric flasks- appropriate volumes

6.6 Graduated cylinder-appropriate volume

6.7 Pipettes

6.8 Analytical balance

6.9 Top-loading balance

7.0 REAGENTS
Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability*.

7.1 Reagent water-lab generated deionized water. ASTM Type I or Type II. The conductivity must be checked daily in accordance with SOP AN35: *Conductivity Checks for Laboratory Deionized Water*.

7.2 Nitric acid (HNO_3)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals. Each lot of acid must be assayed in the laboratory to ensure that each particular lot can be used for trace analysis.

7.3 Hydrochloric acid (HCl)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals. Each lot of acid must be assayed in the laboratory to ensure that each particular lot can be used for trace analysis.

7.4 Extraction solution_ Add ~500mL of reagent water, 55.5mL of concentrated HNO_3, and 167.5mL of concentrated HCl to a 1.0-L volumetric flask. Dilute to volume with reagent water.

8.0 STANDARDS

The preparation of the spiking solutions must be tracked in accordance with SOP AN41: *Standard Material Traceability.* General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation.*

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation.

8.1 ICP Matrix Spiking Solution 1 is a solution purchased from SPEX. The catalogue number is SPIKE-1. Store this solution at room temperature. Prepare this solution every six months or sooner if needed or required.

8.2 Preparation of the ICP Matrix Spiking Solution 2

Add 20-mL to 30-mL of reagent water to a clean100-mL volumetric flask. Add 1-mL of concentrated nitric acid (HNO_3) and 5-mL of hydrochloric acid (HCl) to the volumetric flask. The standard will have an acid concentration of 1% HNO_3 and 5% HCl when diluted to volume.

Add the volumes of the stock standards given in the following table to the volumetric flask:

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

Dilute to a final volume of 100-mL with reagent water. Store the standard at room temperature. Prepare this solution every six months or sooner if needed or required.

9.0 SAMPLE PREPARATION

This digestion procedure is used for the preparation of filter material for the determination of total metals by ICP. This digestion procedure is not suitable for some analytes that will be analyzed by graphite furnace atomic absorption (GFAA) because HCl can cause interferences during furnace atomization.

Wear gloves during this entire procedure. Do not touch the exposed area of the filter.

9.1 Place the sample filter paper on a plastic or inert surface with the exposed side up (the side with the particulate material-this will usually be the side with the sample identification number). A sheet of plastic wrap (e.g., Saran Wrap) may be used to cover the surface.

9.2 Place two wooded rulers on each lengthwise side of the filter paper, parallel to each other. The rulers must not touch the particulate material but should be positioned so that they contact the filter paper about ½ inch from the side.

9.3 Place a straight edge on the two rulers-the straight edge will be above but must not touch the particulate material. Place the straight edge in the middle of the filter paper, perpendicular tot he rulers. Using a stainless steel razor, cut the filter paper. Move the straight edge one inch and make a second cut. This will result in a 1" x 8" strip.

Cut a 1" x 8" strip for the blank and for the LCS. The same filter may be used and two 1" x 8" strips taken from the same 8" x 10" filter.

9.4 Carefully transfer the strips to labeled digestion vessels.

9.5 Add 1.0-mL of the appropriate spiking solution to the designated laboratory control spike.

9.6 Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the weight of sample digested
- batch identification
- fume hood #
- temperature of the hot plate or digestion block (daily)
- the lot number of the acids used for the digestion
- the lot number of the ICP spiking solutions
- the time that the digestion was started
- the SOP/method number

9.7 Add 10mL of extraction solution (7.4) to each digestion vessel. The acid solution must cover the strip completely. If the acid does not cover the strip, add reagent water so that the strip is immersed in liquid. Mix gently and cover the beaker with a watchglass.

9.8 Carefully heat the beaker until a gentle reflux is achieved-the sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker. Do not allow the samples to boil. Reflux for 30 minutes.

9.9 Remove the beakers from the hot plate or digestion block and allow the beakers to cool to room temperature. Add 10mL of reagent water and allow the sample to stand for 30 minutes.

9.10 Wash down the inside of the beaker and the watchglass with reagent water. Filter and dilute the sample digestate to a final volume of 20mL with reagent water.

9.11 Record the analyst's initials, the final volume of the sample digestate, and the date that the digestion was completed in the digestion logbook. The sample is now ready for analysis.

10.0 PROCEDURES

The digestion procedure is described in Section 9.0. The analytical procedure is given in SOP ME 70: *Elements by ICP.*

11.0 CALCULATIONS

Calculations for the determination of metals by ICP in the sample digest are given in SOP ME70: *Elements by ICP*. The calculation of metals on the filter follows:

$$Mass(ug) = Cdigest \otimes F \otimes DF \otimes 9$$

Mass(ug) = mass of metal in micrograms
Cdigest = concentration of the metal in the digest (ug/L)
F = final volume of the digest in liters(L)
DF = dilution factor
9 = multiplier for strip of filter-a 1" x 8" strip is one ninth of the exposed area of the filter paper

The sample is then corrected for the blank. If the metal is not detected in the blank, then Mb = 0.

$$Mass(corr) = Ms - Mb$$

where
M(corr) = mass of metal in sample corrected for blank (ug)
Ms = mass of metal in sample uncorrected for bank(ug)
Mb = mass of metal in blank (ug)

12.0 QUALITY CONTROL/QUALITY ASSURANCE

The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank and a lab control standard (LCS).

SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch. The accuracy and precision limits are published in the current LQM.

13.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

The temperature of the hot plate or digestion block must be monitored daily. If the temperature required for sample preparation cannot be maintained the heating device must be removed from service and repaired or replaced.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digestates must be disposed in accordance with SOP CA70: *Waste Management*.

15.0 REFERENCES

Compendium Method IO-3.0: Selection, Preparation, and Extraction of Filter Material. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, June 1999, published by the Center for Environmental Research Information, Office of Research and Development, USEPA< Cincinnati, OH..

ELEMENTS BY ICP (200.7 and 601) UNCONTROLLED COPY

Approved by:

R. Wayne Potts — 21 March 2001
Date

Title: Technical Manager, QA

STL X Savannah ___ Tallahassee ___ Mobile ___ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures to determine the concentration of various elements by inductively coupled plasma (ICP) atomic emission spectroscopy. This method contains the analytical procedures for the determination of metals in surface and ground water, wastewater, soil, sediment, leachate (EP or TCLP), and waste samples after digestion.

1.2 Table 1 lists the elements that may be determined by ICP and the characteristic wavelength used for each element. The reporting limit (RL) for each element, the method detection limit (MDL) for each element, and the accuracy and precision criteria for each element are in the Laboratory Quality Manual (LQM) prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Prior to analysis by ICP, the sample must be solubilized or digested using the sample preparation method appropriate to the matrix. Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and exited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT). The PMTs, located behind the exit slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

2.2 Definitions

ICP -inductively coupled (argon) plasma; sometimes referred to a "ICAP"
TCLP-toxicity compound leaching procedure
EP (tox)-extraction procedure (toxicity)
Analytical Spike or Post-Digestion Spike - addition of a known concentration of analyte to an aliquot of sample after the preparation steps have been performed
RL - reporting limit, the lowest calibration standard or the sample equivalent of the lowest calibration standard; published in LQM or project-specific quality assurance plan (QAPP); sometimes referred to as the "practical quantitation limit(PQL).
MDL - method detection limit, the concentration that can be reported with 99% confidence that the result is greater than zero; published in LQM

2.3 This method is based on EPA Method 200.7 and SW-846 Method 6010B. Note that EPA has promulgated two versions of method 200.7-one for NPDES samples and one for drinking water. The calibration sequence for drinking water by 200.7 requires a multi-point curve with a minimum of three standards and a calibration blank.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.3 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.4 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses, the safe handling instructions for these compounds, and first aid instructions.

4.0 INTERFERENCES

4.1 Spectral interferences are caused by (1) the overlap of a spectral line from another element, (2) unresolved overlap of molecular band spectra, (3) background contribution from continuous phenomena, and (4) stray light from the line emissions of highly concentrated elements.

4.1.1 Spectral overlap may be compensated for by the use of inter-element correction factors.

4.1.2 Background contribution and stray light can be compensated for by a background correction adjacent to the analyte line.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity can cause significant inaccuracies, especially in samples containing high concentrations of dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample digestate, by using a peristaltic pump, or by using the method of standards additions(MSA), or use of an internal standard

4.3 Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

5.1 Aqueous Samples

5.1.1 Liquid samples are routinely collected in 250-mL or 500-mL plastic containers. The sample is preserved with HNO_3 to a pH <2. The sample must be digested and analyzed within 6 months of collection. Samples may be stored at room temperature.

5.1.2 Samples for dissolved metals should be filtered in the field before acid is added to the sample. If the sample is to be filtered in the lab, no preservative is added to the sample until the sample is filtered.

5.2 Soil/Sediment Samples
Soil and sediment samples are routinely collected in 500-mL plastic containers. The sample is iced at the time of collection and is stored in the lab at 4C (less than 6C but not frozen) until time of digestion and analysis. The sample must be digested and analyzed within 6 months of collection.

5.3 TCLP or EP Toxicity Leachate Samples
The leachate is transferred to a plastic container after the extraction procedure. The sample is preserved with HNO_3 to a pH <2. The leachate sample must be digested and analyzed within 6 months of completion of the leaching procedure.

5.4 Waste Samples
Waste samples are routinely collected in 500-mL plastic containers. The sample must be digested and analyzed within 6 months of collection.

6.0 APPARATUS AND MATERIALS

6.1 Thermo Jarrell Ash TJA ICAP61E-trace, or other suitable inductively coupled plasma emission spectrometer with data system

6.2 Argon gas supply and appropriate fittings

6.3 Cooling water supply

6.4 Peristaltic pump

6.5 Volumetric flasks

6.6 Pipettes

7.0 REAGENTS

Reagents are tracked in accordance with STL SOP AN44:*Reagent Traceability.*

7.1 Reagent water-lab generated deionized water, ASTM Type I or Type II. The conductivity is monitored in accordance with STL SOP AN35.

7.2 Nitric acid (HNO_3)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.4 Hydrochloric acid (HCl)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions or from stock solutions purchased from vendors. Certificates of analysis or purity must be received with all neat compounds or stock solutions. All preparation steps must be in accordance with STL SOP AN41: *Standard Materials Traceability.* SOP AN43 contains guidance for the preparation of standards.

8.1 Recommended concentrations for the calibration standards are given in Table 1. Appendix A contains examples for the preparation of the initial calibration and calibration verification standards for both 6010 and 200.7. if the laboratory uses "recipes' other than those listed in Appendix A, the recipe must be documented in the standard material traceability logbook or as controlled posting. All standards must have be prepared in 5% hydrochloric acid and 1% nitric acid by volume.

NOTE: Standards must be prepared every six months "or sooner if needed or required." "If needed" means the standard has been exhausted; "if required" means that the standard does not meet the QC criteria.

8.2 Preparation of the Linearity Check Solutions

The linearity check solutions are prepared individually according to the following equation:

$$Vs = \frac{Vlc \otimes Clc}{Cs}$$

where
Vs = volume of stock standard (mL)
Cs = concentration of stock standard (mg/L)
Vlc = volume of linearity check standard to prepare (mL)
Clc = concentration of linearity check standard to prepare (mg/L)

The linearity check solutions are prepared at the concentrations specified in Table 1. Prepare sufficient volume to perform the linearity check, maintaining the hydrochloric acid concentration at 5% by volume and the nitric acid concentration at 1% by volume.

9.0 SAMPLE PREPARATION

The sample preparation and digestion procedures are listed in the following SOPs:

MATRIX	SOP
Aqueous and leachate samples	ME50
Soils and Sediments	ME51
Wastes and oils	ME51

10.0 ANALYSIS PROCEDURE

The analytical sequence, including standardization and calibration verification, is included in the SOP Summary in Appendix A. The SOP Summary also included the acceptance criteria for QC, including recommended corrective actions.

10.1 Initial Calibration/Standardization

10.1.1 Turn the ICP on and allow it to become thermally stable before beginning to analyze the calibration standards. It will take about an hour for the instrument to warm up. If optics were turned off, allow 2 hours warm up time.

10.1.2 Run the "Automatic Profile" program. The "automatic profile" of the instrument should be checked twice a day to compensate for changes in air pressure, humidity, and temperature. If the environment of the instrument is such that daily changes in the instrument profile are extreme, the instrument should be "profiled" every few hours.

10.1.3 Analyze the calibration standards and calibrate the ICP. ***If using a multi-point calibration, use the Calibration/Analysis and Curvefit programs to calibrate the instrument.***

10.1.4 The highest concentration calibration standard is reanalyzed after the instrument is standardized as an "unknown". The results for the re-analysis of the highest concentration calibration standard must be within +/- 5% of the true value for each target analyte. If the result for any target analyte is outside of this range, the ICP may need to be "profiled" and the standardization/calibration repeated.

10.1.5 The QC Check standards (ICV) and the Calibration Blank (ICB) are analyzed as a check on the instrument calibration.

10.1.5.1 (EPA Method 6010) The results for the target compounds in the initial calibration verification (ICV) must be within the +/- 10 % of the true value.

10.1.5.2 (EPA Method 200.7) The results for the target compounds in the initial calibration verification (ICV) must be within the +/-5.0 % of the true value. **When performing 200.7 work, note that this solution should be prepared fresh weekly.**

10.1.5.3 (EPA 6010/200.7) The results for the target compounds in the initial calibration blank (ICB) must be less than the RL.

10.1.6 The RL/PQL Check Solution is analyzed to demonstrate that the ICP is capable of detecting the target compounds at or near the reporting limit (RL). The determined concentration must within +/- 50% of the true concentration.

10.1.7 The ICP Interference Check Sample is analyzed. The concentrations of the target analytes must be within 20% of the true concentrations. Pay particular attention to false positives and false negatives for elements not present in the interference check solutions.

10.2 Continuing Calibration Verification (CCV)

10.2.1 The calibration of the ICP must be verified every 10 samples by the analysis of the analysis of the QC Check Solutions (CCV) and the Calibration Blank (CCB).

10.2.1.2 (EPA Method 6010/200.7-DW) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/- 10 % of the true value.

10.2.1.2 (EPA Method 200.7-NPDES) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/-5.0 % of the true value.

10.2.1.3 (EPA 6010/200.7) The results for the target compounds in the continuing calibration blank (CCB) must be less than the Reporting Limit (RL).

10.2.2 ICP Interference Check Solution and the RL check solution are analyzed at the beginning and end of each analytical sequence.

10.3 Sample Analysis

10.3.1 The samples are analyzed only after the ICB/CCB and ICV/CCV criteria are met.

10.3.2 The samples are analyzed in a sequence as follows:

INSTRUMENT WARM-UP
PROFILE
INITIAL CALIBRATION (STANDARDIZATION/CALIBRATION OF THE ICP)
REANALYSIS OF HIGH CONCENTRATION CALIBRATION STANDARD AS A SAMPLE
INITIAL CALIBRATION VERIFICATION (ICV)
INITIAL CALIBRATION BLANK (ICB)
DETECTION LIMIT CHECK SOLUTION
ICP INTERFERENCE CHECK SOLUTION A (ICSA)
ICP INTERFERENCE CHECK SOLUTION AB (ICSAB)
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB

The analytical sequence must end with the analysis of the detection limit check standard, ICSA, ICSAB, CCV and CCB. The 10 samples include all QC samples/standards with the exception of CCVs and CCBs.

10.3.3 Determine the concentration of the samples and QC items using the procedures of Section 11.

10.3.3.1 If the concentration of a sample is above the linear range of the ICP, the sample digestate must be diluted and reanalyzed.

10.3.3.2 The amount of sample digestate needed to prepare the desired dilution is determined form the following equation:

$$V_{digest} = \frac{Vf_{vol}}{DF}$$

where
Vf_{vol} = final volume of diluted sample (mL)
V_{digest} = volume of sample digestate used to make the dilution (mL)

10.3.3.3 The dilution factor is calculated as follows:

$$DF = \frac{Vf_{vol}}{V_{digest}}$$

where
Vf_{vol} = final volume of diluted sample extract (mL)
V_{digest} = volume of sample extract used to make the dilution (mL)

NOTE: The following examples are based on a final volume of 100mL. It may be more convenient to prepare dilutions at smaller final volumes.

EXAMPLE
A sample digestate is analyzed and one of the target analytes exceeds the linear range of the ICP. 1.0mL of the digestate is added to a 100mL volumetric flask and the extract brought up to volume with reagent water. What is the dilution factor?

$$DF = \frac{100mL}{1.0mL} = 100$$

Dilutions must be prepared in reagent water containing 5% hydrochloric acid and 1% nitric acid by volume.

Some samples may require multiple dilutions; that is, a dilution of a dilution will have to be made. In this case, the final dilution factor is the product of the individual dilutions.

10.4 Dilution QC Check
A dilution is prepared and analyzed on one sample per batch to determine if matrix interferences are present.

10.4.1 Select a sample digestate that contains one or more target analytes at a concentrations greater than 10X the reporting limit.

10.4.2 Dilute the digestate by a factor of 5 (DF=5) and analyze the dilution using the same procedures used for the un-diluted aliquot.

10.4.3 Compare the results of the diluted and un-diluted aliquots of sample digestate.

10.4.4 If the results of the dilution are within ± 10% of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than ± 10%, a matrix interference should be suspected and the sample digestate should be subjected to a post-digestion spike (see section 10.4).

If the concentration of the analyte in the sample is not at least 50 times the instrument detection limit, evaluate the post-digestion spike.

10.5 Post-digestion Spike QC Check
A post-digestion spike is performed on one sample per analytical batch to determine if matrix interferences are present. This post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration is not at least 50 times the instrument detection limit. This should be the same sample selected for dilution in 10.3, above.

10.5.1 Transfer 10mL of a digestate to a suitable vial.

10.5.2 Spike the sample with 0.10mL of ICP Matrix Spike I and 0.10mL of ICP Matrix Spike II. The theoretical concentration of the post digestion spike is the same as the LCS or MS if the volume of spiking solution is discounted.

10.5.3 Analyze the spiked aliquot and an un-spiked aliquot (the un-spiked may have been analyzed previously and does not need to be reanalyzed).

10.5.4 Calculate the percent recovery of the post digestion spike:

$$\%REC = \frac{C_{ps} - C_s}{C_2} \times 100$$

where

Cps = concentration of post digestion spike (ug/L)
Cs = concentration of un-spiked sample (ug/L)
C2 = theoretical concentration of spike (ug/L)
(See 10.2.5.2)

10.5.5 Evaluate the recovery using the following decision matrix. Limits for post digestion spikes are 75-125% recovery.

Result of Post Digestion Spikes	Action
Within 75-125% limits	None
>125% recovery	Repeat analysis. Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample
<75% recovery but >50% recovery	1) Dilute and re-spike. Elevate RL accordingly (for all associated samples). 2) Spike and evaluate all associated samples. 3) Spike and evaluate all associated samples by single point MSA 4) Qualify all associated samples
<50% recovery	Dilute digestate and repeat spike. Treat all samples associated with spike in the same manner as the spiked sample (i.e., spike or dilute samples) If recoveries are not 75-125%, analyze all associated samples by single point MSA. Note – high level of target analytes may inhibit spike recovery. Consult the supervisor in events where high levels of targets appear to be interfering

Note: The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high if corrected for spike recovery.

10.5.6 The post digestion spike and the method of standard additions must not be applied to samples analyzed at a dilution that produces a significant negative response. The analyst must use good judgement when evaluating data where the sample response is negative. Where a significant negative response is present, the digestate should be diluted and reanalyzed to determine the extent of the matrix interferences.

10.6 Single Point Method of Standard Additions
Two identical aliquots of the sample digest, Vx, are taken. One aliquot is spiked with a solution of known concentration, Cs. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The concentration of both aliquots are measured and the sample concentration, Cx, is calculated:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

where

S_1 = absorbance or concentration of the spiked aliquot
S_2 = absorbance or concentration of the un-spiked aliquot
Vs = Volume of spike solution

Example:		
	Sample concentration (S_2):	523 ug/L.
	Spike solution concentration (C_s):	50,000 ug/L
	Volume of spike solution (V_s):	0.10mL
	Volume of sample aliquots (V_x):	10mL
	Spiked sample concentration (S_1):	951 ug/L

C_x = [(523)*(0.10)*(50,000)]/[(951-523)*10)] = [2,615,000]/[4280] = 611 ug/L

10.7 Determination of Linear Range of the ICP
The linear range must be determined a minimum of once per year. Divisions performing CLP analyses are required to determine and document the linear range quarterly. Documentation of the linear range study must be kept on hand and be available for inspection. A summary of the linear range study must be available to the bench analyst.

10.7.1 Profile and calibrate the ICP as described in Section 10.1

10.7.2 Prepare individual standards at concentrations that are expected to define the linear range of the instrument. Use the concentrations in Table 1 for guidance. The calibration standards and the linear range standards should be matrix matched; that is, they have the same percentage of hydrochloric and nitric acids.

10.7.3 Analyze the standards following the analytical sequence described in Section 10.3. Verify the calibration after every 10 analyses.

10.7.4 Compare the concentration of the linear range standard with its true concentration.

$$PercentDifference = \left| \frac{Ccal - Ctrue}{Ctrue} \right| \otimes 100$$

where
Ccal = concentration determined from analysis
Ctrue = true concentration of the standard

If the percent difference is less than or equal to 5%, the linear range is confirmed at that concentration. If the percent difference is greater than 5%, repeat the analysis with a lower concentration.

The linear range may be extended by analyzing higher standards and evaluating the results against the 5% difference criterion. The linear range of the ICP for an analyte is the highest standard of that analyte that meets this criterion.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Aqueous and Leachate Samples

Aqueous samples are routinely reported in mg/L while the ICP is routinely calibrated in ug/L. If the results are reported in ug/L, the conversion factor is omitted from the calculation.

11.1.1 The concentration of the target analyte in liquid samples is calculated as follows:

$$Concentration\,(mg/L) = ug/L(from\ printout) \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)-usually 50mL (0.050L)
V = volume of sample digested (L)
DF = dilution factor

11.1.2 The Reporting Limit (RL) of the target analyte in liquid samples is calculated as follows:

$$Concentration(mg/L) = RLqap \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
RLqap = reporting limit from STL LQM (ug/L)
F = final volume of the sample digestate (L)
V= volume of sample digested (L)
DF = dilution factor

The LQM Reporting Limits assumes:
F = 50mL, V = 50mL, and DF = 1

11.2 Soil/Solid Samples

Soils and solids are routinely reported in mg/kg while the ICP is routinely calibrated in ug/L. If the results are reported in ug/kg, the conversion factor is omitted from the calculation.

11.2.1 The concentration of the target analyte in soil and solid samples is calculated as follows:

$$Concentration(mg/kg,dw) = ug/L(from\ printout) \otimes \frac{F}{W \otimes solids} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)
W = volume of sample digested (kg)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)
(for example, if the percent solids is 85%, the decimal equivalent is 0.85; if the %solids is 100%, the decimal equivalent is 1.0.)

11.2.2 The Reporting Limit (RL) of the target analyte in soil/solid samples is calculated as follows:

$$Concentration(mg/kg,dw) = RL_{qap} \otimes \frac{0.0010kg}{W \otimes solids} \otimes \frac{F}{0.100L}\ x\ DF$$

where
RL(qap) = reporting limit from LQM
W = weight of sample digested (kg)
F = final volume of the sample digestate (L)
V = volume of sample digested (L)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)

The LQM Reporting Limits assumes F = 0.100L (100mL), DF = 1, W = 0.0010kg (1.0g), and solids = 1.0

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 STL SOP AN02: *Analytical Batching* and the SOP Summary provide guidance on evaluating QC and sample data, including recommended corrective actions.

12.2 The method detection limit (MDL) is determined annually in accordance with STL SOP CA90. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP.

12.3 Determination of the Instrument Detection Limit (IDL)

The difference between the MDL and the IDL is the *digestion step*. The MDL samples are prepared and digested prior to analysis. The IDL is defined as three times the standard deviation of seven replicate analyses analyzed over three non-consecutive days. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP. See SOP CA91 for the procedures for the determination of the IDL.

12.4 The linear range of the ICP must be determined at least annually. The procedure for the determination is given in Section 10.7 of this SOP. If any calibration regression fit, other than linear, is utilized for the calibration of the ICP (i.e., Curvilinear or Full Fit), the upper limit of the linear range is the concentration of the High Standard.

12.5 Interelement correction factors (IEC) for all elements must be determined annually. Use the manufacturer's guidance for determination of the IECs. The IECs must be verified at the beginning and end of each analytical sequence.

13.0 TROUBLESHOOTING AND PREVENTIVE MAINTENANCE

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	**Service Interval**							**SERVICE LEVEL**
	D	**W**	**M**	**Q**	**SA**	**A**	**AN**	
ICAP								
Pump Tubing	X							Change.
Nebulizer							X	Clean.
Filters			X					Inspect monthly, clean or replace as needed.
Spray Chamber							X	Clean.
Quartz Torch							X	Clean and realign.

D = daily W = Weekly M = monthly Q = Quarterly SA = semi-annually A = annually AN = as needed

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digests must be disposed of in accordance with SOP CA70:*Waste Management*.

15.0 REFERENCES

15.1 *Methods for Chemical Analysis of Water and Waste*; U.S EPA Office of Research and Development: Cincinnati, OHIO, March 1983.

15.2 *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986.

15.3 *Methods for the Determination of Metals in Environmental Samples*; US EPA Office of Research and Development. Washington, DC.

TABLE 1

Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Aluminum (Al)	308.215	10	1.0/5.0	0.20	800	2.0	200
Antimony (Sb)	206.838	10	1.0/0.50	0.020	10	0.50	50
Arsenic (As)	189.042 193.696	1.0	1.0/0.50	0.010	25	2.0	200
Barium (Ba)	493.409	10	1.0/5.0	0.010	10	2.0	200
Beryllium (Be)	313.042	1.0	1.0/0.50	0.0040	10	0.050	5.0
Boron (B)	249.678	10	1.0/5.0	0.050	100	1.0	100
Cadmium (Cd)	226.502 228.802	1.0	1.0/5.0	0.0050	10	0.050	5.0
Calcium (Ca)	317.933 315.887	10	1.0/5.0	0.50	800	5.0	500
Chromium (Cr)	267.716	10	1.0/5.0	0.010	25	0.20	20
Cobalt (Co)	228.616	1.0	1.0/0.50	0.010	25	0.50	50
Copper (Cu)	324.754	10	1.0/5.0	0.020	50	0.25	25
Iron (Fe)	259.940 271.441	10	1.0/5.0	0.050	800	1.0	100
Lead (Pb)	220.353	1.0	1.0/0.50	0.0050	5	0.50	50
Magnesium (Mg)	279.079	10	1.0/5.0	0.50	1000	5.0	500

TABLE 1							
Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Manganese (Mn)	257.610	10	1.0/5.0	0.010	50	0.50	50
Molybdenum (Mo)	202.030	1.0	1.0/0.50	0.010	50	0.50	50
Nickel (Ni)	231.604	5.0	1.0/2.5	0.040	10	0.50	50
Potassium (K)	766.491	20	10/5.0	1.0	50	5.0	500
Selenium (Se)	196.026	10	1.0/5.0	0.010	25	2.0	200
Silver (Ag)	328.068	1.0	1.0/5.0	0.010	5.0	0.050	5.0
Sodium (Na)	588.995 330.231	10	1.0/5.0	0.50	20	5.0	500
Strontium (Sr)	421.552	10	1.0/5.0	0.010	100	0.50	50
Thallium (Tl)	189.042 190.801 377.572	10	1.0/5.0	0.010	30	2.0	200
Tin (Sn)	189.989	10	1.0/5.0	0.050	50	1.0	100
Titanium (W)	334.941	10	1.0/5.0	0.010	10	1.0	100
Vanadium (V)	292.402	10	1.0/5.0	0.010	50	0.50	50
Zinc (Zn)	213.856 206.200+	5.0	1.0/2.5	0.020	20	0.50	50

*For guidance only-instrument sensitivity will vary.

APPENDIX A
SOP SUMMARY

METHOD SUMMARY - ICP ANALYSIS

HOLD/STORAGE

Container	Minimum 250mL plastic bottle with plastic or Teflon-lined lid
Preservative	HNO3 to pH <2 in the field. If dissolved metals are required, filter the samples before preservation.
Storage	Liquids preserved to pH <2 may be stored at room temperature until preparation. Solid samples must be stored at 4C (less than 6C but not frozen) until preparation.
Hold Time	Samples must be analyzed within six months from the time of collection.

SAMPLE PREPARATION

Samples should be prepared with the appropriate matrix-specific procedure.

ANALYTICAL SEQUENCE

Ignite Plasma	Follow instrument manufacturer's guidelines and allow instrument to stabilize for at least 60 minutes.
Profile Instrument	Follow manufacturer's guidelines.
Initial Calibration	Calibrate with a blank and a high standard or a blank and three standards. Verify calibration by reanalyzing highest concentration standard for each element.
Initial Calibration Verification (ICV/ICB)	Analyze an initial calibration verification solution at the beginning of the run. ICV solution must come from a source other than the calibration standard source. Analyze a calibration blank after the ICV.
Continuing Calibration Verification (CCV/CCB)	Analyze a standard with concentrations at or near mid-range levels of the calibration. The CCV should be analyzed every 10 samples and at the end of the analysis run Analyze a continuing calibration blank after every CCV.
Interference Check Solutions	At the beginning and the end of an analysis run, verify the inter-element and background corrections by analyzing the interferent check solutions (ICSA & ICSAB).
Detection limit check solution	At the beginning and the end of an analysis run and verify the accuracy at the RL by analyzing a solution at the SL RL
Serial Dilution	Perform serial dilution (1/5) on a representative sample from each batch..
Post Digestion Spike Recovery.	To check for possible matrix interference, analyze a post digestion spike on a representative sample (minimum of 1 per batch). The post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration in the sample is not at least 50 times the instrument detection limit.

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	1 std. and 1 blank	
Initial Calibration: Multi-point-minimum 3 stds and 1 blank	Daily	Correlation ≥0.995	Recalibrate
Highest Standard	Immediately after every calibration	Recoveries within ± 5% of expected values	New initial calibration
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	SW846 = within ±10% 200.7 = within ± 5%	Recalibrate
Continuing Calibration Verification Standard (CCV)	At the beginning and end of the analysis, and every 10 samples	Within ±10% of the true value, 200.7-NPDES - within ± 5% 200.7-Drinking Water – within ±10%	Terminate the analysis, fix the problem and reanalyze the previous 10 samples.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be less that the RL/CRDL	Terminate the analysis, correct the problem and reanalyze the previous 10 samples
Interference check standards (ICSA/ICSAB)	At the beginning and end of an analysis run	Determined values must be within ± 20% of the true values. Pay attention to false positives and false negatives for elements not present in the solutions.	Terminate the analysis, correct the problem, recalibrate, and reanalyze all samples since the last ICS that was in control.
Lab control sample	One per batch of twenty samples or less	6010B: STL LQM 200.7: 85-115%	Redigest and reanalyze batch
Preparation blank - SW846	One per batch of twenty samples or less	|result| <RL or result <5% of the analyte level in the sample.	Redigest and reanalyze batch
Preparation blank - 200.7	One per batch of twenty samples or less	|result| <RL or result <10% of the analyte level in the sample	Redigest and reanalyze batch
MS/MSD - SW846	One set per batch of twenty samples or less	STL LQM	Flag and report data
Serial Dilution (1/5 Dilution)	One per batch of twenty samples or less	See section 10.3.4	
Post Digestion Spike	One per batch of twenty samples or less	See section 10.4.5	
Detection Limit Check Solution	At the beginning and end of an analysis run	Recovery +/-50% of the true concentration.	Stop the analysis, fix the problem and reanalyze the affected samples.

APPENDIX B
EXAMPLES OF STANDARD PREPARATION

GENERAL INSTRUCTIONS

All calibration standards must contain 5% hydrochloric acid and 1% nitric acid by volume. The following table lists the volume of each acid needed to prepare the desired final volume of standard.

Final Volume of Standard (mL)	Volume of Hydrochloric acid (mL)	Volume of Nitric Acid (mL)
100	5.0	1.0
200	10	2.0
500	25	5.0
1000	50	10

For example, to prepare 500mL of a standard:

- Add 100mL to 200mL of reagent water to a clean 500mL volumetric flask.
- Add 5.0mL of concentrated nitric acid (HNO_3) and 25mL of hydrochloric acid (HCl) to the volumetric flask.
- Add the volumes of the stock standards given in the table to the volumetric flask:
- Dilute to a final volume of 500mL with reagent water. Store the standard at room temperature.

SINGLE POINT CALIBRATION STANDARDS FOR 6010

Calibration Standard 1-Calibration Blank (ICB, CCB)

Add 500mL to 600mL of reagent water to a clean 1-L volumetric flask. Add 10mL of concentrated nitric acid (HNO_3) and 50mL of hydrochloric acid (HCl) to the volumetric flask. Dilute to a final volume of 1.0-L with reagent water. Store the standard at room temperature. Other volumes may be prepared at the discretion of the lab. The nitric acid concentration must be 1% by volume and the hydrochloric acid concentration must be 5% by volume.

Calibration STANDARD 2

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (ml)	Conc. of Cal Std (mg/L)
Silver(Ag)	1000	0.50	500	1.0
Arsenic(As)	1000	0.50		1.0
Molybdenum(Mo)	1000	0.50		1.0
Lead(Pb)	1000	0.50		1.0
Selenium(Se)	1000	5.0		10
Antimony(Sb)	1000	0.50		1.0
Thallium(Tl)	1000	5.0		10

Calibration STANDARD 3

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Beryllium(Be)	1000	0.50	500	1.0
Barium(Ba)	1000	5.0		10
Cadmium(Cd)	1000	0.50		1.0
Cobalt(Co)	1000	0.50		1.0
Chromium(Cr)	1000	5.0		10
Copper(Cu)	1000	5.0		10
Manganese(Mn)	1000	5.0		10
Nickel(Ni)	1000	2.5		5.0
Zinc(Zn)	1000	2.5		5.0

Calibration STANDARD 4

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum(Al)	10000	0.50	500	10
Iron(Fe)	10000	0.50		10
Boron(B)	1000	5.0		10
Strontium(Sr)	1000	5.0		10
Titanium (Ti)	1000	5.0		10

Calibration STANDARD 5

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Calcium(Ca)	10000	0.50	500	10
Potassium(K)	10000	1.0		20
Magnesium(Mg)	10000	0.50		10
Sodium(Na)	10000	0.50		10
Tin(Sn)	1000	5.0		10
Vanadium(V)	1000	5.0		10

MULTI-POINT INSTRUMENT CALIBRATION-200.7

For all drinking water samples (EPA 200.7) the ICP must be calibrated with a minimum of three standards and a blank. The following standards may be used for this purpose. With the Thermo Jarrell Ash software the Calibration Analysis and Curve-fit programs must be used to be successful with the multi-point calibration of the ICP instruments.

High Standard.

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum (Al)	10000	1.0	1000	10
Antimony (Sb)	1000	1.0		1.0
Arsenic (As)	1000	1.0		1.0
Boron (B)	1000	10		10
Barium (Ba)	1000	10		10
Beryllium (Be)	1000	1.0		1.0
Cadmium (Cd)	1000	1.0		1.0
Calcium (Ca)	10000	1.0		10
Cobalt (Co)	1000	1.0		1.0
Chromium (Cr)	1000	10		10
Copper (Cu)	1000	10		10
Iron (Fe)	10000	1.0		10
Lead (Pb)	1000	1.0		10
Magnesium (Mg)	10000	1.0		10
Manganese (Mn)	1000	10		10
Molybdenum Mo)	1000	1.0		1.0
Nickel (Ni)	1000	5.0		5.0
Potassium (K)	10000	1.0		10
Selenium (Se)	1000	10		10
Silver (Ag)	1000	1.0		1.0
Sodium (Na)	10000	1.0		10
Strontium (Sr)	1000	10		10
Thallium (Tl)	1000	10		10
Tin (Sn)	1000	10		10
Titanium (Ti)	1000	10		10
Vanadium (V)	1000	10		10
Zinc (Zn)	1000	5.0		5.0

Mid-Level Standard- Prepare as the CCV is prepared.

Low-Level Standard- Prepare as the RL/PQL Check Standard.

Initial Calibration Verification (ICV) Solution

Element/Stock	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
SPEX QC19	(1)	5.0	500	(2)
SPEX QC 7	(1)	5.0		(2)
Tin(Sn)	1000	0.50		1.0
Strontium (Sr)	1000	0.50		1.0
Potassium (K)	10000	0.50		10(3)
Sodium (Na)	10000	0.45		10(3)

(1) SPEX QC19 and SPEX QC7 are solutions containing multiple elements. The concentrations are given on the certificate of analysis.

(2) The final concentrations of the various elements are the same as listed in Table 1. The SPEC QC solutions are diluted by a factor of 100 from the concentration listed on the certificate of analysis.

(3) These concentrations include the contribution from SPEX Solutions QC-7

Continuing Calibration Verification (CCV) Standard

(also used as midpoint of multi-point calibration for EPA 200.7)

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
Aluminum (Al)	10000	0.50	1000	5.0
Antimony (Sb)	1000	0.50		0.50
Arsenic (As)	1000	0.50		050
Boron (B)	1000	5.0		5.0
Barium (Ba)	1000	5.0		5.0
Beryllium (Be)	1000	0.50		0.50
Cadmium (Cd)	1000	0.50		0.50
Calcium (Ca)	10000	0.50		5.0
Cobalt (Co)	1000	0.50		0.50
Chromium (Cr)	1000	5.0		5.0
Copper (Cu)	1000	5.0		5.0
Iron (Fe)	10000	0.50		5.0
Lead (Pb)	1000	0.50		0.50
Magnesium (Mg)	10000	0.50		5.0
Manganese (Mn)	1000	5.0		5.0
Molybdenum (Mo)	1000	0.50		0.50
Nickel (Ni)	1000	2.5		2.5
Potassium (K)	10000	0.50		5.0
Selenium (Se)	1000	5.0		5.0
Silver (Ag)	1000	0.50		0.50
Sodium (Na)	10000	0.50		5.0
Strontium (Sr)	1000	5.0		5.0
Thallium (Tl)	1000	5.0		5.0
Tin (Sn)	1000	5.0		5.0
Titanium (Ti)	1000	5.0		5.0
Vanadium (V)	1000	5.0		5.0
Zinc (Zn)	1000	2.5		2.5

Reporting Limit (RL) Check Standard

(also used as low point in multi-point calibrations; e.g. EPA 200.7)

Preparation of RL/PQL Stock A-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Silver (Ag)	1000	0.10	100	1.0
Arsenic (As)	1000	0.10		1.0
Cadmium (Cd)	1000	0.050		0.50
Copper (Cu)	1000	0.20		2.0
Nickel (Ni)	1000	0.40		4.0
Lead (Pb)	1000	0.050		0.50
Selenium (Se)	1000	0.10		1.0
Thallium (Tl)	1000	0.10		1.0

Preparation of RL/PQL Stock B-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Aluminum (Al)	10000	0.20	100	20
Boron (B)	1000	0.50		5.0
Barium (Ba)	1000	0.10		1.0
Beryllium (Be)	1000	0.040		0.40
Calcium (Ca)	10000	0.50		50
Cobalt (Co)	1000	0.10		1.0
Chromium (Cr)	1000	0.10		1.0
Iron (Fe)	10000	0.050		5.0
Magnesium (Mg)	10000	0.50		50
Manganese (Mn)	1000	0.10		1.0
Molybdenum Mo)	1000	0.10		1.0
Sodium (Na)	10000	0.50		50
Antimony (Sb)	1000	0.20		2.0
Strontium (Sr)	1000	0.10		1.0
Tin (Sn)	1000	0.50		5.0
Titanium (Ti)	1000	0.10		1.0
Vanadium (V)	1000	0.10		1.0
Zinc (Zn)	1000	0.20		2.0

Preparation of RL/PQL Stock C-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume of Cal Std	Conc. Of Stock Std
Potassium(K)	10000	1.0	100	100

Preparation of the RL/PQL Check Solution-ICP

RL/PQL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A-ICP	5.0	500
Stock B-ICP	5.0	
Stock C-ICP	5.0	

ICP Interference Check Solutions

Preparation of ICP Interference Check Solution A

Element	Conc. Of Stock(mg/L)	mL of Stock Std	Final Volume(mL)	Conc. (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200

Preparation of ICP Interference Check Solution AB

Element	Conc. of Stock(mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200
Silver (Ag)	1000	0.10		0.20
Arsenic (As)	1000	0.050		0.10
Barium (Ba)	1000	0.25		0.50
Beryllium (Be)	1000	0.25		0.50
Cadmium (Cd)	1000	0.50		1.0
Cobalt (Co)	1000	0.25		0.50
Chromium (Cr)	1000	0.25		0.50
Copper (Cu)	1000	0.25		0.50
Manganese (Mn)	1000	0.25		0.50
Nickel (Ni)	1000	0.50		1.0
Lead (Pb)	1000	0.025		0.050
Antimony (Sb)	1000	0.30		0.60
Selenium (Se)	1000	0.025		0.050
Thallium (Tl)	1000	0.050		0.10
Vanadium (V)	1000	0.25		0.50
Zinc (Zn)	1000	0.50		1.0
Molybdenum (Mo)	1000	0.50		1.0
Tin (Sn)	1000	0.50		1.0

ICP Matrix Spiking Solutions

ICP Matrix Spiking Solution 1 is a solution purchased from SPEX. The certificate of analysis will list the concentrations of the analytes. Store this solution at room temperature. Prepare this solution every six months or sooner if needed or required.

Preparation of the ICP Matrix Spiking Solution 2

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

IDL/MDL Solution

The IDL/MDL solution is used in this procedure for two purposes:

1) To determine the Instrument Detection Limit (IDL) of each target compound on a quarterly basis (SOP CA91); and
2) To determine the Method Detection Limit (MDL) of each target compound on an annual basis (SOP CA90). MDLs should be digested straight and at 1:2 dilutions.

Preparation of IDL/MDL Stock A

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Silver (Ag)	1000	0.040	100	0.40
Arsenic (As)	1000	0.20		2.0
Barium (Ba)	1000	0.020		0.20
Beryllium (Be)	100	0.050		0.050
Cadmium (Cd)	1000	0.040		0.40
Lead (Pb)	1000	0.10		1.0
Antimony (Sb)	1000	0.20		2.0
Selenium (Se)	1000	0.20		2.0
Thallium (Tl)	1000	0.20		2.0

Preparation of IDL/MDL Stock B

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. Of Std. (mg/L)
Cobalt (Co)	1000	0.030	100	0.30
Chromium (Cr)	1000	0.10		1.0
Copper (Cu)	1000	0.10		1.0
Manganese (Mn)	1000	0.020		0.20
Molybdenum (Mo)	1000	0.040		0.40
Nickel (Ni)	1000	0.10		1.0
Tin (Sn)	1000	0.20		2.0
Vanadium (V)	1000	0.060		0.60
Zinc (Zn)	1000	0.10		1.0

Preparation of IDL/MDL Stock C

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Aluminum (Al)	10000	0.10	100	10
Calcium (Ca)	10000	0.10		10
Iron (Fe)	10000	0.10		10
Magnesium (Mg)	10000	0.10		10
Potassium (K)	10000	0.20		20
Sodium (Na)	10000	0.040		4.0

IDL/MDL Solution

Preparation of IDL/MDL Stock D

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron(B)	1000	0.40	100	4.0
Strontium (Sr)	1000	0.040		0.40
Titanium (Ti)	1000	0.050		0.50
Sodium (Na)	10000	2.0		200

Preparation of the IDL/MDL Check Solution

IDL/MDL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A	5.0	1000
Stock B	5.0	
Stock C	5.0	
Stock D	5.0	

The IDL/MDL Check Solution contains the following elements at the given concentrations:

Element	Concentration(mg/L)
Be	0.00025
Ba, Mn	0.0010
Co	0.0015
Ag, Cd, Mo, Sr	0.0020
Ti	0.0025
V	0.0030
Cr, Cu, Ni, Pb, Zn	0.0050
As, Sb, Se, Sn, Tl	0.010
Na(1), B	0.020
Ca, Fe, Mg	0.050
Al, K	0.10
Na	1.0

(1) If the wavelength for sodium is 588.995, the lower concentration (0.020mg/L) is used for the IDL./MDL check solution. In this case, only stocks A,B, and C are used to make the IDL/MDL Check Solution. IDL/MDL Check Solutions for B, Sr, and Ti are prepared and evaluated separately.

1.0 PRINCIPLE AND APPLICABILITY

1.1 An air sampler, properly located at the measurement site, draws a measured quantity of ambient air into a covered housing and through a filter during a 24-hr (nominal) sampling period. The sampler flow rate and the geometry of the shelter favor the collection of particles up to 25-50 μm (aerodynamic diameter), depending on wind speed and direction. The filters used are specified to have a minimum collection efficiency of 99 percent for 0.3 μm (DOP) particles.

1.2 The filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain. The total volume of air sampled, corrected to EPA standard conditions (25° C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of total suspended particulate matter in the ambient air is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed in micrograms per standard cubic meter (μg/std m3). For samples collected at temperatures and pressures significantly different than standard conditions, these corrected concentrations may differ substantially from actual concentrations (micrograms per actual cubic meter), particularly at high elevations. The actual particulate matter concentration can be calculated from the corrected concentration using the actual temperature and pressure during the sampling period.

2.0 INHERENT SOURCES OF ERROR

2.1 Airflow variation. The weight of material collected on the filter represents the (integrated) sum of the product of the instantaneous flow rate times the instantaneous particle concentration. Therefore, dividing this weight by the average flow rate over the sampling period yields the true particulate matter concentration only when the flow rate is constant over the period. The error resulting from a non-constant flow rate depends on the magnitude of the instantaneous changes in the flow rate and in the particulate matter concentration. Normally, such errors are not large, but they can be greatly reduced by equipping the sampler with an automatic flow controlling mechanism that maintains constant flow during the sampling period. Use of a constant flow controller is recommended.

2.2 Air volume measurement. If the flow rate changes substantially or non-uniformly during the sampling period, appreciable error in the estimated air volume may result from using the average of the pre-sampling and post-sampling flow rates. Greater air volume measurement accuracy may be achieved by (1) equipping the sampler with a flow controlling mechanism that maintains constant air flow during the sampling period, (2) using a calibrated, continuous flow rate recording device to record the actual flow rate during the

sampling period and integrating the flow rate over the period, or (3) any other means that will accurately measure the total air volume sampled during the sampling period. Use of a continuous flow recorder is recommended, particularly if the sampler is not equipped with a constant flow controller.

2.3 Loss of volatiles. Volatile particles collected on the filter may be lost during subsequent sampling or during shipment and/or storage of the filter prior to the post-sampling weighing. Although such losses are largely unavoidable, the filter should be reweighed as soon after sampling as practical.

2.4 Artifact particulate matter. Artifact particulate matter can be formed on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air, resulting in a higher than true TSP determination. This effect usually occurs early in the sample period and is a function of the filter pH and the presence of acid gases. It is generally believed to account for only a small percentage of the filter weight gain, but the effect may become more significant where relatively small particulate weights are collected.

2.5 Humidity. Glass fiber filters are comparatively insensitive to changes in relative humidity, but collected particulate matter can be hygroscopic. The moisture conditioning procedure minimizes but may not completely eliminate error due to moisture.

2.6 Filter handling. Careful handling of the filter between the pre-sampling and post-sampling weightings is necessary to avoid errors due to loss of fibers or particles from the filter. A filter paper cartridge or cassette used to protect the filter can minimize handling errors

2.7 Non-sampled particulate matter. Particulate matter may be deposited on the filter by wind during periods when the sampler is inoperative. It is recommended that errors from this source be minimized by an automatic mechanical device that keeps the filter covered during non-sampling periods, or by timely installation and retrieval of filters to minimize the non-sampling periods prior to and following operation.

2.8 Timing errors. Samplers are normally controlled by clock timers set to start and stop the sampler at midnight. Errors in the nominal 1,440-min sampling period may result from a power interruption during the sampling period or from a discrepancy between the start or stop time recorded on the filter information record and the actual start or stop time of the sampler. Such discrepancies may be caused by (1) poor resolution of the timer set-points, (2) timer error due to power interruption, (3) missetting of the timer, or (4) timer malfunction. In general, digital electronic timers have much better set-point resolution than mechanical timers, but require a battery backup system to maintain continuity of

operation after a power interruption. A continuous flow recorder or elapsed time meter provides an indication of the sampler run-time, as well as indication of any power interruption during the sampling period and is therefore recommended.

2.9 Recirculation of sampler exhaust. Under stagnant wind conditions, sampler exhaust air can be re-sampled. This effect does not appear to affect the TSP measurement substantially, but may result in increased carbon and copper in the collected sample. This problem can be reduced by ducting the exhaust air well away, preferably downwind, from the sampler.

3.0 PRECISION AND BIAS

3.1 The high-volume sampling procedure used to collect ambient air particulate matter has a between-laboratory relative standard deviation of 3.7 percent over the range 80 to 125 µg/m3. The combined extraction-analysis procedure has an average within-laboratory relative standard deviation of 5 to 6 percent over the range 1.5 to 15 µg metals/ml, and an average between laboratory relative standard deviation of 7 to 9 percent over the same range. These values include use of either extraction procedure.

4.0 APPARATUS

4.1 Filter.

4.1.1 Size: 20.3±0.2xK25.4±0.2 cm (nominal 8xK10 in).

4.1.2 Nominal exposed area: 406.5 cm2 (63 in\2\).

4.1.3 Material: Glass fiber or other relatively inert, non-hygroscopic material.

4.1.4 Collection efficiency: 99 percent minimum as measured by the DOP test (ASTM-2986) for particles of 0.3µm diameter.

4.1.5 Recommended pressure drop range: 42-54 mm Hg (5.6-7.2 kPa) at a flow rate of 1.5 std m3/min through the nominal exposed area.

4.1.6 pH: 6 to 10.

4.1.7 Integrity: 2.4 mg maximum weight loss.

4.1.8 Pinholes: None.

4.1.9 Tear strength: 500 g minimum for 20 mm wide strip cut from filter in weakest dimension. (See ASTM Test D828-60).

4.1.10 Brittleness: No cracks or material separations after single lengthwise crease.

4.2 Sampler. The air sampler shall provide means for drawing the air sample, via reduced pressure, through the filter at a uniform face velocity.

4.2.1 The sampler shall have suitable means to:

a. Hold and seal the filter to the sampler housing.

b. Allow the filter to be changed conveniently.

c. Preclude leaks that would cause error in the measurement of the air volume passing through the filter.

d. Manually adjust the flow rate to accommodate variations in filter pressure drop and site line voltage and altitude. The adjustment may be accomplished by an automatic flow controller or by a manual flow adjustment device. Any manual adjustment device must be designed with positive detents or other means to avoid unintentional changes in the setting.

4.2.2 Minimum sample flow rate, heavily loaded filter: 1.1 m3/min (39 ft3/min).

4.2.3 Maximum sample flow rate, clean filter: 1.7 m3/min (60 ft3/min).K

4.2.4 Blower Motor: The motor must be capable of continuous operation for 24-hr periods.

4.3 Sampler shelter.

4.3.1 The sampler shelter shall:

a. Maintain the filter in a horizontal position at least 1 m above the sampler supporting surface so that sample air is drawn downward through the filter.

b. Be rectangular in shape with a gabled roof.

c. Cover and protect the filter and sampler from precipitation and other weather.

d. Discharge exhaust air at least 40 cm from the sample air inlet.

e. Be designed to minimize the collection of dust from the supporting surface by incorporating a baffle between the exhaust outlet and the supporting surface.

4.3.2 The sampler cover or roof shall overhang the sampler housing somewhat and shall be mounted so as to form an air inlet gap between the cover and the sampler housing walls. This sample air inlet should be approximately uniform on all sides of the sampler. The area of the sample air inlet must be sized to provide an effective particle capture air velocity of between 20 and 35 cm/sec at the recommended operational flow rate. The capture velocity is the sample air flow rate divided by the inlet area measured in a horizontal plane at the lower edge of the cover. Ideally, the inlet area and operational flow rate should be selected to obtain a capture air velocity of 25 ±2 cm/sec.

4.4 Flow rate measurement devices.

4.4.1 The sampler shall incorporate a flow rate measurement device capable of indicating the total sampler flow rate. Two common types of flow indicators covered in the calibration procedure are (1) an electronic mass flow meter and (2) an orifice or orifices located in the sample air stream together with a suitable pressure indicator such as a manometer, or aneroid pressure gauge. A pressure recorder may be used with an orifice to provide a continuous record of the flow. Other types of flow indicators (including rotameters) having comparable precision and accuracy are also acceptable.

4.4.2 The flow rate measurement device must be capable of being calibrated and read in units corresponding to a flow rate which is readable to the nearest 0.02 std m3/min over the range 1.0 to 1.8 std m3/min.

4.5 Thermometer, to indicate the approximate air temperature at the flow rate measurement orifice, when temperature corrections are used.

4.5.1 Range: -40° to +50° C (223-323 K).

4.5.2 Resolution: 2° C (2 K).

4.6 Barometer, to indicate barometric pressure at the flow rate measurement orifice, when pressure corrections are used.

4.6.1 Range: 500 to 800 mm Hg (66-106 kPa).

4.6.2 Resolution: #5 mm Hg (0.67 kPa).

4.7 Timing/control device.

4.7.1 The timing device must be capable of starting and stopping the sampler to obtain an elapsed run-time of 24 hr ±1 hr (1,440 ±60 min).

4.7.2 Accuracy of time setting: #30 min, or better

4.8 Flow rate transfer standard, traceable to a primary standard

4.8.1 Approximate range: 1.0 to 1.8 m3/min.

4.8.2 Resolution: 0.02 m3/min.

4.8.3 Reproducibility: #2 percent (2 times coefficient of variation) over normal ranges of ambient temperature and pressure for the stated flow rate range.

4.8.4 Maximum pressure drop at 1.7 std m3/min; 50 cm H2O (5 kPa).

4.8.5 The flow rate transfer standard must connect without leaks to the inlet of the sampler and measure the flow rate of the total air sample.

4.8.6 The flow rate transfer standard must include a means to vary the sampler flow rate over the range of 1.0 to 1.8 m3/min (35-64 ft3/min) by introducing various levels of flow resistance between the sampler and the transfer standard inlet.

4.8.7 The conventional type of flow transfer standard consists of: An orifice unit with adapter that connects to the inlet of the sampler, a manometer or other device to measure orifice pressure drop, a means to vary the flow through the sampler unit, a thermometer to measure the ambient temperature, and a barometer to measure ambient pressure. A preferable design has a variable flow restriction that can be adjusted externally without disassembly of the unit. Use of a conventional, orifice-type transfer standard is assumed in the calibration procedure.

4.9 Filter conditioning environment

4.9.1 Controlled temperature: between 15° and 30° C with less than ±3° C variation during equilibration period.

4.9.2 Controlled humidity: Less than 50 percent relative humidity, constant within ±5 percent.

4.10 Analytical balance.

4.10.1 Sensitivity: 0.1 mg.

4.10.2 Weighing chamber designed to accept an unfolded 20.3 x 25.4 cm (8 x 10 in) filter.

4.11 Area light source, similar to X-ray film viewer, to backlight filters for visual inspection.

4.12 Numbering device, capable of printing identification numbers on the filters before they are placed in the filter-conditioning environment, if not numbered by the supplier.

5.0 REAGENTS

5.1 Glass fiber filters. The specifications given below are intended to aid the user in obtaining high quality filters with reproducible properties.

5.1.1 Metals content. The absolute metals content of filters is not critical, but low values are, of course, desirable. EPA typically obtains filters with a metals content of 75 µg/filter.

It is important that the variation in lead content from filter to filter, within a given batch, be small.

5.1.2 Testing.

5.1.2.1 For large batches of filters (500 filters) select at random 20 to 30 filters from a given batch. For small batches (500 filters) a lesser number of filters may be taken. Cut one 3/4''x8'' strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in sections 7 and 8.

5.1.2.2 Calculate the total metal in each filter as

Fb = ug Metals/ml x 100ml/strip x 12 strips/filter

where:

Fb = Amount of lead per 72 square inches of filter, µg.

5.1.2.3 Calculate the mean, Fb, of the values and the relative standard deviation (standard deviation/mean x 100). If the relative standard deviation is high enough so that, in the analyst's opinion, subtraction of Fb, may result in a significant error in the µg Pb/m3, the batch should be rejected.

5.1.2.4 For acceptable batches, use the value of Fb to correct all lead analyses of particulate matter collected using that batch of filters. If the analyses are below the LDL no correction is necessary.

6.0 Calculation.

6.1 Determine the average sampler flow rate during the sampling period according to either 6.1.1 or 6.1.2 below.

6.1.1 Determine Qstd for the initial flow rate from the sampler calibration curve, either graphically or from the transposed regression equation:

Qstd = 1/m([Appropriate expression from table 2]-b)

Similarly, determine Qstd from the final flow reading, and calculate the average flow Qstd as one-half the sum of the initial and final flow rates.

6.1.2 For a sampler with a continuous flow recorder, determine the average flow rate device reading, I, for the period. Determine Qstd from the sampler calibration curve, either graphically or from the transposed regression equation:

Qstd = 1/m([Appropriate expression from table 2]-b)

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals and calculating an average reading before determining Qstd.

6.2 Calculate the total air volume sampled as:

V-Qstd(t)

Where V = total air volume sampled, in standard volume units (std m3);
Qstd = average standard flow rate, std m3/min.; and
T = sampling time, min.

6.3 Calculate and report the particulate matter concentration as:

$$TSP = \frac{(Wf - Wi)10\text{^}6}{v}$$

where:

TSP = mass concentration of total suspended particulate matter, µg/std m3;
Wi = initial weight of clean filter, g;
Wf = final weight of exposed filter, g;
V = air volume sampled, converted to standard conditions, std m3,
10^6 = conversion of g to µg.

6.4 If desired, the actual particulate matter concentration can be calculated as follows:

$$(TSPa = TSP(P3 / Pstd')(298 / T3)$$

where:

(TSP)a = actual concentration at field conditions, µg/m3;
TSP = concentration at standard conditions, µg/std m3;
P3 = average barometric pressure during sampling period, mm Hg;
Pstd = 760 mn Hg (or 101 kPa);
T3K = average ambient temperature during sampling period, K.

7.0 Quality Control

¾ inch x 8 inch glass fiber filter strips containing 80 to 2000 µg metals/strip (as metals salts) and blank strips with zero metal content should be used to determine if the method-as being used-has any bias. Quality control charts should be established to monitor differences between measured and true values. The frequency of such checks will depend on the local quality control program.

8.0 Procedure

8.1 Number each filter, if not already numbered, near its edge with a unique identification number.

8.2 Backlight each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.

8.3 Equilibrate each filter in the conditioning environment for at least 24-hr.

8.4 Following equilibration, weigh each filter to the nearest milligram and record this tare weight (Wi) with the filter identification number.

8.5 Do not bend or fold the filter before collection of the sample.

8.6 Open the shelter and install a numbered, pre-weighed filter in the sampler, following the sampler manufacturer's instructions. During inclement weather, precautions must be taken while changing filters to prevent damage to the clean filter and loss of sample from or damage to the exposed filter. Filter cassettes that can be loaded and unloaded in the laboratory may be used to minimize this problem.

8.7 Close the shelter and run the sampler for at least 5 min to establish run-temperature conditions.

8.8 Record the flow indicator reading and, if needed, the barometric pressure (P3) and the ambient temperature (T3) see NOTE following step 8.12). Stop the

sampler. Determine the sampler flow rate; if it is outside the acceptable range (1.1 to 1.7 m3/min [39-60 ft3/min]), use a different filter, or adjust the sampler flow rate. Warning: Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate recalibration.

8.9 Record the sampler identification information (filter number, site location or identification number, sample date, and starting time).

8.10 Set the timer to start and stop the sampler such that the sampler runs 24-hrs, from midnight to midnight (local time).

8.11 As soon as practical following the sampling period, run the sampler for at least 5 min to again establish run-temperature conditions.

8.12 Record the flow indicator reading and, if needed, the barometric pressure (P3) and the ambient temperature (T3).

Note: No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flow meter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration. For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site during the sampling period should be estimated from weather bureau or other available data.

8.13 Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions. Touch only the outer edges of the filter. See the precautions in step 8.6.

8.14 Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).

8.15 Record the ending time or elapsed time on the filter information record, either from the stop set-point time, from an elapsed time indicator, or from a continuous flow record. The sample period must be 1,440 ± 60 min. for a valid sample.

8.16 Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be

pertinent to the measurement. If the sample is known to be defective, void it at this time.

8.17 Equilibrate the exposed filter in the conditioning environment for at least 24-hrs.

8.18 Immediately after equilibration, reweigh the filter to the nearest milligram and record the gross weight with the filter identification number.

9.0 Calibration.

9.1 Calibration of the high volume sampler's flow indicating or control device is necessary to establish traceability of the field measurement to a primary standard via a flow rate transfer standard.

Note: The following calibration procedure applies to a conventional orifice-type flow transfer standard and an orifice-type flow indicator in the sampler (the most common types). For samplers using a pressure recorder having a square-root scale, other acceptable calibration procedures may apply. Other types of transfer standards may be used if the manufacturer or user provides an appropriately modified calibration procedure.

9.2 Certification of the flow rate transfer standard.

9.2.1 Equipment required: Positive displacement standard volume meter traceable to the National Bureau of Standards (such as a Roots meter or equivalent), stop-watch, manometer, thermometer, and barometer.

9.2.2 Connect the flow rate transfer standard to the inlet of the standard volume meter. Connect the manometer to measure the pressure at the inlet of the standard volume meter. Connect the orifice manometer to the pressure tap on the transfer standard. Connect a high-volume air pump (such as a high-volume sampler blower) to the outlet side of the standard volume meter.

9.2.3 Check for leaks by temporarily clamping both manometer lines (to avoid fluid loss) and blocking the orifice with a large-diameter rubber stopper, wide cellophane tape, or other suitable means. Start the high-volume air pump and note any change in the standard volume meter reading. The reading should remain constant. If the reading changes, locate any leaks by listening for a whistling sound and/or retightening all connections, making sure that all gaskets are properly installed.

9.2.4 After satisfactorily completing the leak check as described above, unclamp both manometer lines and zero both manometers.

9.2.5 Achieve the appropriate flow rate through the system, either by means of the variable flow resistance in the transfer standard or by varying the voltage to the air pump. At least five different but constant flow rates, evenly distributed, with at least three in the specified flow rate interval (1.1 to 1.7 m3/min [39-60 ft\3\/min]), are required.

9.2.6 Measure and record the certification data on a standard form according to the following steps.

9.2.7 Observe the barometric pressure and record as P1.

9.2.8 Read the ambient temperature in the vicinity of the standard volume meter and record it as T1.

9.2.9 Start the blower motor, adjust the flow, and allow the system to run for at least 1 min for a constant motor speed to be attained.

9.2.10 Observe the standard volume meter reading and simultaneously start a stopwatch. Record the initial meter reading (Vi).

9.2.11 Maintain this constant flow rate until at least 3 m3 of air have passed through the standard volume meter. Record the standard volume meter inlet pressure manometer reading as ˆP, and the orifice manometer reading as ˆH. Be sure to indicate the correct units of measurement.

9.2.12 After at least 3 m3 of air have passed through the system, observe the standard volume meter reading while simultaneously stopping the stopwatch. Record the final meter reading (Vf) and the elapsed time (t).

9.2.13 Calculate the volume measured by the standard volume meter at meter conditions of temperature and pressures as Vm=Vf-Vi.

9.2.14 Correct this volume to standard volume (std m3) as follows:

$$Vstd = Vm \frac{P1 - dP}{Pstd} \frac{Tstd}{T1}$$

where:

Vstd = standard volume, std m3;
Vm = actual volume measured by the standard volume meter;
P1 = barometric pressure during calibration, mm Hg or kPa;
DP = differential pressure at inlet to volume meter, mm Hg or kPa;
Pstd = 760 mm Hg or 101 kPa;
Tstd = 298 K;
T1 = ambient temperature during calibration, K.

Calculate the standard flow rate (std m3/min) as follows:

$$Qst = \frac{Vstd}{t}$$

where:

Qstd = standard volumetric flow rate, std m3/min
t = elapsed time, minutes.

Record Qstd to the nearest 0.01 std m3/min.

9.2.15 Repeat steps 9.2.9 through 9.2.14 for at least four additional constant flow rates, evenly spaced over the approximate range of 1.0 to 1.8 std m3/min (35-64 ft\3\/min).

9.2.16 For each flow, compute

¤(5)•H (P1/Pstd)(298/T1)

and plot these value against Qstd. Be sure to use consistent units (mm Hg or kPa) for barometric pressure. Draw the orifice transfer standard certification curve or calculate the linear least squares slope (m) and intercept (b) of the certification curve:

¤(6)•H (P1/Pstd)(298/T1)=mQstd+b.

A certification graph should be readable to 0.02 std m3/min.

9.2.17 Recalibrate the transfer standard annually or as required by applicable quality control procedures.

9.3 Calibration of sampler flow indicator.

Note: For samplers equipped with a flow controlling device, the flow controller must be disabled to allow flow changes during calibration of the sampler's flow indicator, or the alternate calibration of the flow controller given in 9.4 may be used. For samplers using an orifice-type flow indicator downstream of the motor, do not vary the flow rate by adjusting the voltage or power supplied to the sampler.

9.3.1 A standard form should be used to record the calibration data.

9.3.2 Connect the transfer standard to the inlet of the sampler. Connect the orifice manometer to the orifice pressure tap. Make sure there are no leaks between the orifice unit and the sampler.

9.3.3 Operate the sampler for at least 5 minutes to establish thermal equilibrium prior to the calibration.

9.3.4 Measure and record the ambient temperature, T2, and the barometric pressure, P2, during calibration.

9.3.5 Adjust the variable resistance or, if applicable, insert the appropriate resistance plate (or no plate) to achieve the desired flow rate.

9.3.6 Let the sampler run for at least 2 min to re-establish the run-temperature conditions. Read and record the pressure drop across the orifice (•H) and the sampler flow rate indication (I).

9.3.7 Calculate ¤(7)H(P2/Pstd)(298/T2) and determine the flow rate at standard conditions (Qstd) either graphically from the certification curve or by calculating Qstd from the least square slope and intercept of the transfer standard's transposed certification curve: Qstd=1/m ¤(8)H(P2/Pstd)(298/T2)-b. Record the value of Qstd.

9.3.8 Repeat steps 9.3.5, 9.3.6, and 9.3.7 for several additional flow rates distributed over a range that includes 1.1 to 1.7 std m3/min.

9.3.9 Determine the calibration curve by plotting values of I against Qstd. The choice of expression from depends on the flow rate measurement device used and also on whether the calibration curve is to incorporate geographic average barometric pressure (Pa) and seasonal average temperature (Ta) for the site to approximate actual pressure and temperature. Where Pa and Ta can be determined for a site for a seasonal period such that the actual barometric pressure and temperature at the site do not vary by more than ±60 mm Hg (8 kPa) from Pa or ±15° C from Ta, respectively, then using Pa and Ta avoids the need for subsequent pressure and temperature calculation when the sampler is used. The geographic average barometric pressure (Pa) may be estimated from an altitude-pressure table or by making an (approximate) elevation correction of -26 mm Hg (-3.46 kPa) for each 305 m (1,000 ft) above sea level (760 mm Hg or 101 kPa). The seasonal average temperature (Ta) may be estimated from weather station or other records. Be sure to use consistent units (mm Hg or kPa) for barometric pressure.

9.3.10 Draw the sampler calibration curve or calculate the linear least squares slope (m), intercept (b), and correlation coefficient of the calibration curve. Calibration curves should be readable to 0.02 std m3/min.

9.3.11 For a sampler equipped with a flow controller, the flow controlling mechanism should be re-enabled and set to a flow near the lower flow limit to allow maximum control range. The sample flow rate should be verified at this time with a clean filter installed. Then add two or more filters to the sampler to see if the flow controller maintains a constant flow; this is particularly important at high altitudes where the range of the flow controller may be reduced.

9.4 Alternate calibration of flow-controlled samplers. A flow-controlled sampler may be calibrated solely at its controlled flow rate, provided that previous operating history of the sampler demonstrates that the flow rate is stable and reliable. In this case, the flow indicator may remain un-calibrated but should be used to indicate any relative change between initial and final flows, and the sampler should be recalibrated more often to minimize potential loss of samples because of controller malfunction.

9.4.1 Set the flow controller for a flow near the lower limit of the flow range to allow maximum control range.

9.4.2 Install a clean filter in the sampler and carry out steps 9.3.2, 9.3.3, 9.3.4, 9.3.6, and 9.3.7.

9.4.3 Following calibration, add one or two additional clean filters to the sampler, reconnect the transfer standard, and operate the sampler to verify that the controller maintains the same calibrated flow rate; this is particularly important at high altitudes where the flow control range may be reduced.

10.0 References.

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TABLE 1. EXPRESSIONS FOR PLOTTING SAMPLER CALIBRATION CURVES

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For incorporation of geographic average pressure and seasonal average temperature
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$\sqrt{I\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$
Rotameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_2}{P_{std}}\right)\left(\frac{298}{T_2}\right)}$	$I\sqrt{\left(\frac{P_2}{P_a}\right)\left(\frac{T_a}{T_2}\right)}$

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.

TABLE 2. EXPRESSIONS FOR DETERMINING FLOW RATE DURING SAMPLER OPERATION

Type of sampler flow rate measuring device	Expression: For actual pressure and temperature corrections	Expression: For use when geographic average pressure and seasonal average temperature have been incorporated into the sampler calibration
Mass flowmeter	I	I
Orifice and pressure indicator	$\sqrt{I\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	$\sqrt{I}$
Rotameter, or orifice and pressure recorder having square root scale*	$I\sqrt{\left(\frac{P_3}{P_{std}}\right)\left(\frac{298}{T_3}\right)}$	I

*This scale is recognizable by its nonuniform divisions and is the most commonly available for high-volume samplers.